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THE CRYSTAL STRUCTURE OF PYROCATECHOL

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The structural formula of pyrocatechol is shown in Fig. 1.

Caspari (1926) obtained the space group of pyrocatechol as $C2/m$ with $a = 17.46$Å, $b = 10.74$Å, $c = 5.4$Å, $\beta = 94° 15'$ and $n = 8$. Kitaigorodskii (1948) found this data incompatible on the basis of the theory of close packing of organic molecules, and redetermined the space group as $P2_1/c$ with $a = 10.15$Å, $b = 5.48$Å, $c = 11.00$Å, $\beta = 118°$ and $n = 4$. Infrared absorption spectra of pyrocatechol in solution show two sharp and nearly equal peaks in the region of O-H fundamental (Davies, 1938) indicating thereby the presence of a weak intramolecular hydrogen bond. Pauling accounted for the two peaks by assuming that one of the two O—H bonds in the molecule is in the cis position and the other in the *trans* position. It was, therefore, of interest to determine the crystal structure and study the nature of hydrogen bonding in the solid state of pyrocatechol.

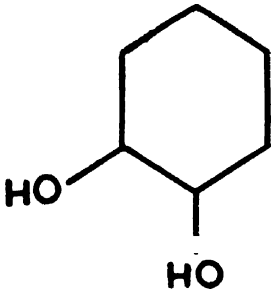

Fig. 1.

The substance is highly hygroscopic and gradually sublimes at room temperature and as such a small single crystal was sealed in a thin-walled glass capillary of .4mm diameter for taking the X-ray photographs. Preliminary investigations confirmed the space group and cell dimensions obtained by Kitaigorodskii. This cell could also be obtained by suitable reduction of the arbitrary unit cell suggested by Caspari.

The short b axis indicated that the (010) projection was likely to be most informative, and thus zero layer Weissenberg photographs about [010] axis using CuKα radiation were taken with different times of exposure, and the relative

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integrated intensities of the spots were estimated visually. The relative intensity data were then placed on the absolute scale by Wilson's statistical method (1942). The atomic scattering factors of carbon and oxygen were taken from Berghuis *et al* (1955) an average isotropic B factor of 3.0 Å^2 was used.

In deducing the trial structure, the pyrocatechol molecule was assumed to be planar with C—OH bond length equal to that of α-resorcinol (Robertson, 1936). Since pyrocatechol contains atoms of nearly the same scattering factors (Carbon and Oxygen), and the (010) projection gives the plane group P2 with only two molecules per effective unit cell, it was considered convenient to make direct use of the Fourier-transform principle (Hanson *et al.*, 1953). The hol weighted reciprocal-lattice section (Fig. 2) shows four prominent peaks on the

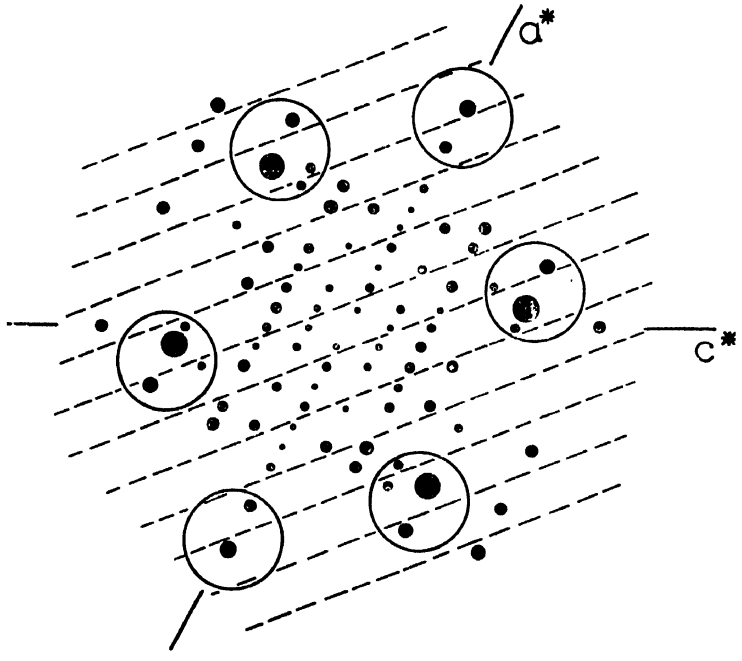

Fig. 2. Hol-section of the weighted reciprocal-lattice of pyrocatechol with broken lines representing the nodal lines of the fringe system. The benzene peaks are indicated by small circles (weight proportional to the unitary structure factors).

'benzene circle' (Taylor, 1952) and two less prominent ones extended beyond it; when joined together by straight lines they make a clear hexagon.

These peaks are, evidently, due to the benzene ring, which forms the nucleus of the molecule, and are less effected by the OH groups, as the centrosymmetrical portion of a molecule has always a stronger influence on its transform than the non-centrosymmetrical portion. The projected shape of the benzene ring was, therefore, obtained from the positions of the peaks, and the tilt of the molecule to the (010) plane was calculaded to be approximately 33°. Careful search of the weighted section also indicates the presence of straight nodal lines of a fringe

system presumably produced by the two centrosymmetric benzene rings in the effective unit cell. From their positions, the coordinates of the centres of the molecules were deduced as $z = 0.9$ Å and $x = 1.6$ Å. The positions of the OH groups were then fixed by trial-and-error method. Taking the coordinates of carbon and oxygen atoms thus obtained the structure factors of all the observed (hol) reflections were calculated. This showed a residual of 40% (approx.). The (010) electron density projection was computed after assigning the calculated phases (signs) to the respective observed structure amplitudes (Fig. 3).

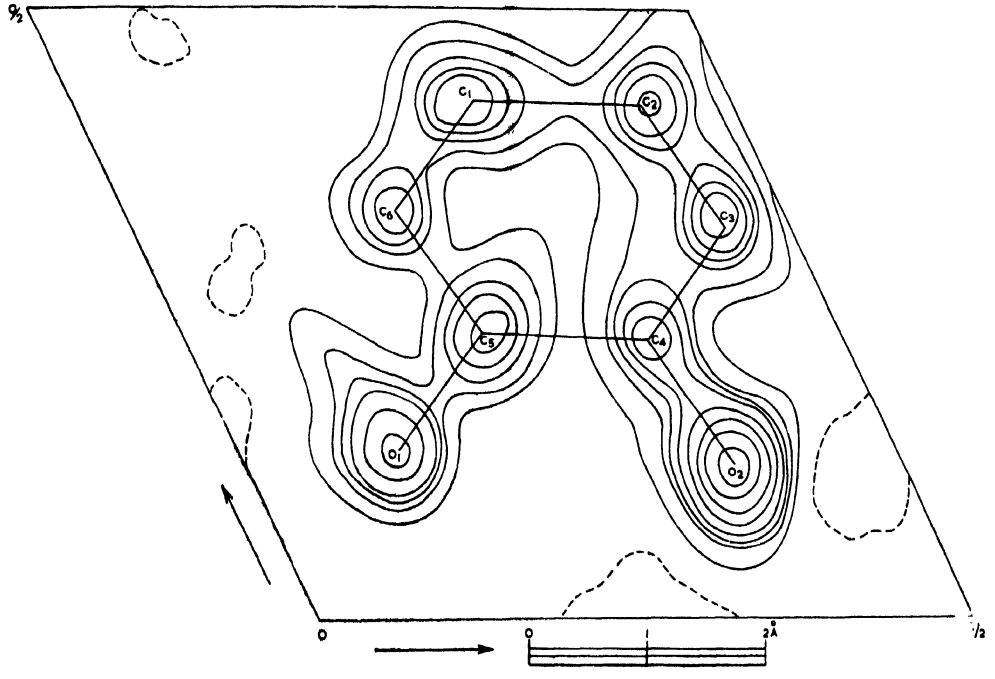

Fig. 3. First (010) electron density projection with contours drawn at arbitrary intervals. Zero-electron contours are shown by broken lines.

TABLE I

Atom	x/a	z/c	Atom	x/a	z/c
C_1	+0.426	+0.302	C_5	+0.230	+0.226
C_2	+0.425	+0.433	C_6	+0.331	+0.203
C_3	+0.328	+0.453	O_1	+0.140	+0.118
C_4	+0.225	+0.356	O_2	+0.125	+0.370

In the electron density map the atoms are well resolved, and the carbon and oxygen peaks are distinguishable. The x and z coordinates (Table I) obtained from the map gave better agreement between the observed and calculated struc-

ture factors, and the R value dropped to 30%. Further refinement is in progress. Details of the investigation will be published shortly.

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